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**Surface-modified effect pigments**

The present invention relates to surface-modified effect pigments having improved applicational properties based on a substrate, where one or more calcined oxide layers, alone or mixed with sulfates, phosphates and/or borates, and an organic coating are applied to the substrate, to processes for the preparation thereof, and to the use thereof.

Plastic parts and surface-coating layers for outdoor applications are often subjected to extreme weather conditions and long-lasting, intense exposure to light over an extended time, resulting in ageing of the materials. This is evident from discoloration, embrittlement and reduced mechanical and chemical stability. The causes thereof are oxidative or photolytic decomposition of the binders or decomposition due to the action of water in liquid form or water vapour. In addition, the pigments employed, in particular pearlescent pigments comprising titanium oxide layers, can also impair the resistance of the application media to the influences of light and weathering. The reason for this lies in the photoactivity of the titanium dioxide layer, which accelerates photolytic decomposition of the organic constituents of the application medium.

In order to inhibit these ageing processes, stabilisers, for example UV light-absorbing substances, are added to formulations for outdoor applications. In addition, the pigments may be provided with further inorganic layers.

Thus, EP 0 644 242 describes polyolefin compositions comprising mica particles coated with titanium dioxide which are coated with one or more layers of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and are calcined. In addition, the composition comprises an antioxidant in order to prevent yellowing.

Besides the photostability, there are other applicational disadvantages on use of effect pigments. Thus, untreated pearlescent pigments are only poorly dispersible in some application media or tend towards agglomeration and the formation of stacks. The agglomerates can only be redispersed with difficulty, with the requisite shear forces potentially resulting in destruction of the thin flakes. A further problem on use of oxidic pearlescent pigments in surface-coating layers is the reduced resistance to condensation. The pearlescent pigment embedded in the organic phase of the surface-coating layer has a polar oxidic surface, onto which water molecules may be adducted. Water vapour diffusing into a layer of this type accumulates at the phase boundary and results in swelling of the boundary layer. A loss in adhesion between the particles and the binder matrix results therefrom, which can result in detachment of the surface-coating layer.

In order to improve the dispersibility, the pigments can be coated with surface modifiers. Thus, WO 99/57204 describes the use of reactive surface modifiers for the preparation of pigments which exhibit good orientation and distribution in the surface coating. However, the pigments obtained in this way prove to be disadvantageous with respect to the photostability.

WO 98/13426 describes the reaction of freshly precipitated oxidic top layers on pearlescent pigments with specific silanes. The post-coating conditions are selected in such a way that freshly precipitated oxide hydrate is always reacted with the organosilanes or even co-precipitation of the metal oxide hydrates with the organosilanes takes place. In the case of pigments coated with hydroxides or oxide hydrates, water may be liberated during processing in plastics, initiating undesired degradation of the polymer chains.

The object was therefore to find surface-modified effect pigments based on substrates which have high resistance to condensation and light. At the

same time, the pigments should be suitable for use in plastic parts and films and be readily dispersible both in aqueous and in non-aqueous media.

- 5 This object is achieved in accordance with the present invention by a surface-modified effect pigment based on a substrate, where one or more calcined oxide layers, alone or mixed with sulfates, phosphates and/or borates, and an organic coating are applied to the substrate.
- 10 Suitable substrates for the present invention are, for example, all known flake-form supports, such as synthetic or natural mica, glass flakes, metal flakes, flake-form  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , or flake-form iron oxide. The metal flakes may consist, inter alia, of aluminium, titanium, bronze, steel or silver, preferably aluminium and/or titanium. The metal flakes may have been
- 15 passivated here by appropriate treatment. In a preferred embodiment, the support may be coated with one or more transparent, semi-transparent and/or opaque layers comprising metal oxides, metal oxide hydrates, metal suboxides, metals, metal fluorides, metal nitrides, metal oxynitrides or mixtures of these materials. The metal oxide, metal oxide hydrate, metal
- 20 suboxide, metal, metal fluoride, metal nitride, metal oxynitride layers or the mixtures thereof can have low refractive indexes (refractive index  $< 1.8$ ) or high refractive indexes (refractive index  $\geq 1.8$ ). Suitable metal oxides and metal oxide hydrates are all metal oxides or metal oxide hydrates known to the person skilled in the art, such as, for example, aluminium oxide, alu-
- 25 minium oxide hydrate, silicon oxide, silicon oxide hydrate, iron oxide, tin oxide, cerium oxide, zinc oxide, zirconium oxide, chromium oxide, titanium oxide, in particular titanium dioxide, titanium oxide hydrate and mixtures thereof, such as, for example, ilmenite or pseudobrookite. Metal suboxides which can be employed are, for example, titanium suboxides. Suitable
- 30 metals are, for example, chromium, aluminium, nickel, silver, gold, titanium, copper or alloys, and a suitable metal fluoride is, for example, magnesium

fluoride. Metal nitrides or metal oxynitrides which can be employed are, for example, the nitrides or oxynitrides of the metals titanium, zirconium and/or tantalum. Preference is given to the application of metal oxide, metal, metal fluoride and/or metal oxide hydrate layers and very particularly preferably metal oxide and/or metal oxide hydrate layers to the support. Furthermore, multilayered structures comprising high- and low-refractive-index metal oxide, metal oxide hydrate, metal or metal fluoride layers may also be present, preferably with high- and low-refractive-index layers alternating. Particular preference is given to layer packages comprising a high-refractive-index layer and a low-refractive-index layer, it being possible for one or more of these layer packages to be applied to the support. The sequence of the high- and low-refractive-index layers can be matched to the support here in order to include the support in the multilayered structure. In a further embodiment, the metal oxide, metal oxide hydrate, metal suboxide, metal, metal fluoride, metal nitride, metal oxynitride layers can be mixed or doped with colorants or other elements. Suitable colorants or other elements are, for example, organic or inorganic coloured pigments, such as coloured metal oxides, for example magnetite, chromium oxide, or coloured pigments, such as, for example, Berlin Blue, ultramarine, bismuth vanadate, Thénard's Blue, or alternatively organic coloured pigments, such as, for example, indigo, azo pigments, phthalocyanines or alternatively Carmine Red, or elements, such as, for example, yttrium or antimony. Effect pigments comprising these layers exhibit a wide variety of colours with respect to their mass tone and can in many cases exhibit an angle-dependent change in the colour (colour flop) due to interference.

In a preferred embodiment, the outer layer on the support is a high-refractive-index metal oxide. This outer layer may additionally be on the above-mentioned layer packages or may be part of a layer package in high-refractive-index supports and can, for example, consist of  $\text{TiO}_2$ , titanium suboxides,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$

and/or mixtures thereof, such as, for example, ilmenite or pseudobrookite.  $\text{TiO}_2$  is particularly preferred.

5 Examples and embodiments of the above-mentioned materials and pigment structures are also given, for example, in Research Disclosures RD 471001 and RD 472005, the disclosure content of which is incorporated herein by way of reference.

10 The thickness of the metal oxide, metal oxide hydrate, metal suboxide, metal, metal fluoride, metal nitride, metal oxynitride layers or a mixture thereof is usually 3 to 300 nm and in the case of the metal oxide, metal oxide hydrate, metal suboxide, metal fluoride, metal nitride, metal oxynitride layers or a mixture thereof is preferably 20 to 200 nm. The thickness of the metal layers is preferably 4 to 50 nm.

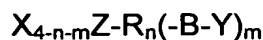
15 In addition, it is also possible to use other substrates, such as, for example, spherical particles or needle-shaped substrates, which may be covered with the above-mentioned layers, in the post-coating according to the invention.

20 For the oxide layer or oxide layers applied to the substrate, the oxides of Al, Si, Zr, Ce, Zn, Fe and/or mixtures thereof are suitable, preference is given to the use of  $\text{Al}_2\text{O}_3$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$  and/or  $\text{SiO}_2$ . Layers of these oxides are distinguished by high transparency, the lack of or a low inherent colour and high gloss, meaning that the colouristic properties of the substrates are not changed. Furthermore, these materials give water-free and chemically inert surfaces after calcination.

25 In addition, mixtures of oxides with sulfates, phosphates and/or borates can also be employed besides the oxides deposited alone. Examples of sulfates are  $\text{ZnSO}_4$ ,  $\text{CaSO}_4$ , examples of phosphates are  $\text{AlPO}_4$ ,  $\text{CePO}_4$ , and an example of borates is  $\text{AlBO}_4$ .

The organic coating applied to the calcined oxide layer acts as coupling reagent and may consist of organosilanes, -aluminates, -titanates and/or zirconates of the general formula

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where X = OH, halogen, alkoxy, aryloxy

Z = Si, Al, Ti, Zr

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R = alkyl, phenyl or hydrogen

B = organic, at least bifunctional group (alkylene, alkyleneoxyalkylene)

Y = amino, substituted amino, hydroxyl, hydroxyalkyl, siloxane, acetoxy, isocyanate, vinyl, acryloyl, epoxide, epoxypropyloxy, imidazole or ureido group

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n, m = 0,1,2,3 where n+m ≤ 3.

The coupling reagents consist of an anchor group ( $X_{4-n-m}Z$ ), which bonds to the surface, at least one hydrophobic group (R,B) and one or more functional group (Y). The coupling reagents are preferably compounds where Z = Si. The anchor group preferably consists of alkoxy silanes, which can be converted into corresponding hydroxyl groups by hydrolytic reaction conditions. The latter can bond to the calcined metal oxide surface and effect anchoring via oxygen bridges. In addition, it is also possible to employ mixtures of various coupling reagents, which can be applied as a mixture or individually.

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The organic coating can be matched to the use medium through the choice of suitable functional groups. In addition, additional bonds between pigment and medium can be formed via the coupling reagent through reaction of the functional groups with corresponding functionalities in the application media. In a particular embodiment, the surface of the pigments according

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to the invention is modified by means of a combination, matched to the use medium, of organic functionalities. Also suitable for this purpose is the use of mixtures of various coupling reagents within the organic coating. The hydrophobicity of the pigment surface can be matched by integration of alkyl-containing coupling reagents, such as, for example, alkylsilanes. Besides the organosilanes, preference is also given to the use of hydrolysates and homogeneous and heterogeneous oligomers and/or polymers thereof, which can likewise be employed alone or in combination with silanes, zirconates, aluminates, zircoaluminates and/or carboxyzirconates as organic coating. Particular preference is given to an organic coating with mixtures of various coupling reagents, in particular with functional groups Y which are different from one another, which ensures a particular range of applications.

Examples of organosilanes are propyltrimethoxysilane, propyltriethoxysilane, isobutyltrimethoxysilane, n-octyltrimethoxysilane, i-octyltrimethoxysilane, n-octyltriethoxysilane, n-decyltrimethoxysilane, dodecyltrimethoxysilane, hexadecyltrimethoxysilane, vinyltrimethoxysilane, preferably n-octyltrimethoxysilane and n-octyltriethoxysilane. Suitable oligomeric, alcohol-free organosilane hydrolysates are, inter alia, the products marketed by Sivento under the trade name "Dynasytan®", such as, for example, Dynasytan HS 2926, Dynasytan HS 2909, Dynasytan HS2907, Dynasytan HS 2781, Dynasytan HS 2776, Dynasytan HS 2627. In addition, oligomeric vinylsilane and also aminosilane hydrolysate are suitable as organic coating. Functionalised organosilanes are, for example, 3-aminopropyltrimethoxysilane, 3-methacryloxytrimethoxysilane, 3-glycidyloxypropyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, gamma-isocyanatopropyltrimethoxysilane, 1,3-bis(3-glycidoxypropyl)-1,1,3,3,-tetramethyldisiloxane, ureidopropyltriethoxysilane, preferably 3-aminopropyltrimethoxysilane, 3-methacryloxytrimethoxysilane, 3-glycidyloxypropyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, gamma-isocyanatopropyltrimethoxysilane. Examples of polymeric silane

systems are described in WO 98/13426 and marketed, for example, by Sivento under the trade name Hydrosil®.

5 The amount of the organic coating is between 0.2 and 5% by weight, based on the pigment, preferably 0.5 to 2% by weight.

10 The object of the present invention is furthermore achieved by a process for the preparation of surface-modified effect pigments, characterised in that a flake-form substrate is coated with one or more oxide layers, alone or mixed with sulfates, phosphates and/or borates, subsequently calcined, and an organic coating is applied.

15 The coating with one or more oxide layers can be carried out both by wet-chemical methods and also via sol-gel processes, the precipitation is preferably carried out by wet-chemical methods. In the case of application by wet-chemical methods, coating with the corresponding oxides, hydroxides and/or oxide hydrates takes place. To this end, the flake-form substrates are suspended in a solvent, preferably water, and solutions of the metal salts are added. The oxides, hydroxides and/or oxide hydrates are precipitated onto the substrates here. Suitable starting compounds are the corresponding halides, nitrates and/or sulfates, use is preferably made of the corresponding halides and/or nitrates. The pH necessary for the precipitation of the respective material is set and optimised by methods known to the person skilled in the art. The sulfates, phosphates and/or borates can be co-precipitated together with the oxides, hydroxides and/or oxide hydrates from suitable metal salts and from corresponding sulfate, phosphate or borate sources. Suitable sulfate sources are sulfuric acid and all soluble sulfates, such as, for example, sodium sulfate, potassium sulfate or lithium sulfate, suitable phosphate sources are phosphoric acid or all soluble phosphates, such as, for example, sodium phosphate, disodium hydrogenphosphate or potassium phosphate, and suitable borate sources are all soluble borates, such as, for example, sodium borate or sodium diborate.

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The amount of the sulfates, phosphates and/or borates and the precipitation conditions, such as, for example, pH or temperature, can be optimised in a manner known to the person skilled in the art. The thickness of the precipitated layer is 0.5-20 nm, preferably 1-10 nm.

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The pigments obtained in this way are subsequently calcined. The calcination can be carried out at temperatures of 250-900°C, preferably at 600-900°C. Through the calcination, the precipitated oxides, hydroxides and/or oxide hydrates are dewatered, converted into the corresponding oxides and compacted.

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After the calcination, the organic coating is applied. The coupling reagents are applied in solution at temperatures above 60°C, preferably above 70°C. Suitable solvents are organic solvents, water or mixtures thereof, water is preferably used. The reaction time necessary for application of the organic coating is at least 5 minutes, it is preferably carried out over a period of 10 to 90 minutes, but can also be extended as desired. The pigment obtained is worked up and isolated by methods familiar to the person skilled in the art, for example by filtration, drying and sieving.

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The surface-modified effect pigments according to the invention are distinguished by improved applicational properties compared with the prior art. The calcination dehydrates and compacts the oxide layers, which results in a reduction in the porosity of the pigment surface. Less water can be absorbed at the compacted surface, and the disadvantageous effects of water adsorbed in the boundary layer can thus be reduced in the surface coating. The calcination also removes water bound chemically in the form of hydroxides or oxide hydrates. This has advantages on use of the pigments in plastics, since water present in thermoplastic polymers, such as, for example, in polyesters, can result in hydrolytic decomposition of the polymer at elevated temperatures. In the case of pigments coated with hydroxides or oxide hydrates, liberation of water can occur during plastics

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processing, initiating undesired degradation of the polymer chains. In the case of the pigments according to the invention, calcination of the oxide layer means that water is also unable to escape during processing of the pigments in plastics, making them particularly suitable for this area of application. The organic coating has a positive influence on the surface properties of the calcined oxide layers. The surfaces post-coated with the organic coating are more hydrophobic and less polar than the untreated oxide surfaces and can thus be wetted better by binders and organic solvents. This results in improved compatibility of the pigments according to the invention with the binder systems used in the application. Furthermore, the organic coating, owing to its steric screening of the pigment surface, inhibits agglomeration of the pigment particles and thus improves their dispersibility.

Surprisingly, the pigments according to the invention exhibit good adhesion of the organic coating to the otherwise chemically resistant oxidic surfaces. This was unexpected, since US 5, 759, 255 teaches that silane coupling reagents are only capable of bonding to freshly precipitated oxide hydrate layers, for example hydrated  $\text{Al}_2\text{O}_3$ . Calcination of the inorganic post-coating is expressly advised against.

Owing to the improved applicational properties, the surface-modified effect pigments described here are suitable for a multiplicity of applications. The invention thus furthermore relates to the use of the surface-modified effect pigments according to the invention for the pigmentation of cosmetics, paints, coatings, printing inks, plastics, films, in security applications, for laser marking, in thermal protection or for colouring seed. The pigments can be incorporated into the respective application media by all methods known to the person skilled in the art.

Printing inks comprising pigments in accordance with the present invention are suitable for all known printing methods, such as, for example, screen printing, flexographic printing, gravure printing or offset printing. The pig-

ments according to the invention are preferably employed in paints, such as, for example, in automotive paints or water-borne coatings, which, owing to the particular stability of the pigments, are suitable for all indoor and outdoor applications. All plastics and films known to the person skilled in the art can advantageously be pigmented with pigments in accordance with the present invention, where the binding of the pigments can take place either purely physically by mixing or chemically through reaction of corresponding functional group in the organic coating with the plastic.

The effect pigments according to the invention are likewise suitable for use in blends with organic dyes and/or pigments, such as, for example, transparent and opaque white, coloured and black pigments, and with flake-form iron oxides, organic pigments, holographic pigments, LCPs (liquid crystal polymers) and conventional transparent, coloured and black lustre pigments based on metal oxide-coated flakes based on mica, glass,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , etc. The effect pigments according to the invention can be mixed with commercially available pigments and fillers in any ratio.

Fillers which may be mentioned are, for example, natural and synthetic mica, nylon powder, pure or filled melamine resins, talc, glasses, kaolin, oxides or hydroxides of aluminium, magnesium, calcium, zinc,  $\text{BiOCl}$ , barium sulfate, calcium sulfate, calcium carbonate, magnesium carbonate, carbon, and physical or chemical combinations of these substances. There are no restrictions regarding the particle shape of the filler. It can be, for example, flake-form, spherical or needle-shaped in accordance with the requirements.

The following examples are intended to explain the invention in greater detail, but without restricting it.

#### Examples:

Example 1

- 100 g of mica flakes having a particle size of 10-50  $\mu\text{m}$  are suspended in 1 l of water and heated to 75°C with stirring. An aqueous 42% solution of 55 g of  $\text{TiCl}_4$  is metered into the suspension over the course of 3 hours, during which the pH is held at 2.2 by addition of dilute sodium hydroxide solution. The mixture is subsequently stirred for a further 30 min. The resultant intermediate comprises about 29% of titanium dioxide (as hydrate), based on the mica proportion.
- The suspension can be worked up to give the desired base pigment, i.e. washed, dried, calcined at 600 to 900°C and subsequently sieved. The pigment is then re-suspended in water and heated to the above-mentioned temperature with stirring. Alternatively, the inorganic post-coating part can be applied directly in the mother suspension.
- The above-mentioned suspension or 129 g of calcined base pigment in 1.3 l of water is heated to 75°C with vigorous stirring, the pH is adjusted to 6.0 using NaOH, and 122 ml of an aluminium chloride\*6  $\text{H}_2\text{O}$  solution (10 g/l) are metered in over the course of 2 hours. During this procedure, the pH is kept constant using sodium hydroxide solution. The mixture is subsequently stirred for at least a further 30 minutes.

- The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 100 to 150°C, the pigment is calcined at 750°C for 30 min and sieved in accordance with the desired particle size.
- The resultant silver-coloured pigment contains a coating comprising 2% of aluminium oxide.

## Organic post-treatment:

- 100 g of the pre-treated pigment are suspended in 1 l of water, the batch is heated to 75°C, and the pH is adjusted to 8.0 using hydrochloric acid or sodium hydroxide solution. 2 g of each of the silanes Dynasylan<sup>®</sup> AMMO, MEMO and GLYMO are added over the course of 10 to 20 minutes, and

the batch is subsequently stirred for a further 60 minutes. The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 120 to 160°C, the pigment is sieved to a particle size of smaller than 40 µm.

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### Example 2

100 g of mica flakes having a particle size of 10-50 µm are suspended in 1 l of water and heated to 75°C with stirring. An aqueous 10% solution of 3.35 g of SnCl<sub>4</sub> is metered into the suspension over the course of one hour, during which the pH is held at 1.8 by addition of dilute sodium hydroxide solution. After a post-stirring time of 30 minutes, an aqueous 42% solution of 237 g of TiCl<sub>4</sub> is metered in over the course of 12 hours, during which the pH is held at 1.8 by addition of dilute sodium hydroxide solution. The mixture is subsequently stirred for a further 30 min. The resultant intermediate comprises about 2% of tin oxide and 100% of titanium dioxide (as hydrate), based on the mica proportion.

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The suspension can be worked up to give the desired base pigment, i.e. washed, dried, calcined at 600 to 900°C and subsequently sieved. The pigment is then re-suspended in water and heated to the above-mentioned temperature with stirring. Alternatively, the inorganic post-coating part can be applied directly in the mother suspension.

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The above-mentioned suspension or 200 g of calcined base pigment in 2.2 l of water are heated to 75°C with stirring, and the pH is adjusted to 3.0 using sodium hydroxide solution or hydrochloric acid. Over the course of 30 minutes, 10% solutions of 2.3 g of CeCl<sub>3</sub> \* 7 H<sub>2</sub>O and 18.9 g of AlCl<sub>3</sub> \* 6 H<sub>2</sub>O are metered in successively. During this procedure, the pH is kept constant using sodium hydroxide solution. After a post-stirring time of 30 minutes, the pH is adjusted to 5 over the course of 60 minutes, and stirring is then continued for a further 30 minutes.

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The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 100 to 150°C, the pigment is calcined at 750°C for 45 min and sieved in accordance with the desired particle size.

5 The resultant pigment contains a coating of 0.5% of cerium oxide and 2% of aluminium oxide.

Organic post-treatment:

10 100 g of the pretreated pigment are suspended in 1 l of water, the batch is heated to 75°C, and the pH is adjusted to 8.0 using hydrochloric acid or sodium hydroxide solution. 2 g of each of the silanes Dynasylan® AMMO, MEMO and GLYMO are added over the course of 10 to 20 minutes, and the mixture is subsequently stirred for a further 60 minutes. The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 120 to 160°C, the pigment is sieved to a particle  
15 size of smaller than 40 µm.

### Example 3

20 The suspension prepared in accordance with Example 2 or 200 g of calcined base pigment in 2.2 l of water is heated to 75°C with stirring, and the pH is adjusted to 3.0 using sodium hydroxide solution or hydrochloric acid. A 10% solution of 15.7 g of  $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$  is metered in over the course of 2 hours with vigorous stirring, during which the pH is kept constant using sodium hydroxide solution. The pH is subsequently adjusted to 5.0 over the  
25 course of 60 minutes, and stirring is then continued for a further 30 minutes.

30 The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 100 to 150°C, the pigment is calcined at 750°C for 45 min and sieved in accordance with the desired particle size.

The resultant pigment contains a coating of 3% of zirconium oxide.

#### Organic post-treatment

100 g of the pretreated pigment are suspended in 1 l of water, the batch is heated to 75°C, and the pH is adjusted to 3.0 using hydrochloric acid or sodium hydroxide solution. 20 ml of a 20% solution of Dynasylan® HS 2929 are added over the course of 10 to 20 minutes, and the mixture is subsequently stirred for a further 30 minutes. The pH is subsequently adjusted to 7.0 over the course of 60 minutes using sodium hydroxide solution. The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 120 to 160°C, the pigment is sieved to a particle size of smaller than 40 µm.

#### Example 4

100 g of rutile-coated silicon dioxide leaves (Colorstream® Viola Fantasy) are heated to 75°C with stirring in 1 l of water, and the pH is adjusted to 4.5 using hydrochloric acid. A 10% solution of 26.1 g of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  is metered in over the course of 2 hours with vigorous stirring, during which the pH is kept constant using sodium hydroxide solution. The pH is subsequently adjusted to 6.5 over the course of 30 minutes, and stirring is continued for a further 30 minutes.

The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 100 to 150°C, the pigment is calcined at 750°C for 45 min and sieved in accordance with the desired particle size.

The resultant pigment contains a coating of 3% of aluminium oxide.

#### Organic post-treatment

500 g of the pretreated pigment are wetted uniformly with 50 ml of a 10% solution of Dynasylan® HS 2926 in a heatable mixer. The mixture is subsequently warmed to 80°C for 2 hours with mixing. After cooling to room temperature, the post-coated pigment is sieved to a particle size of smaller than 40 µm.

### Example 5

5 100 g of rutile-coated aluminium oxide leaves (Xirallic® Sunbeam Gold) are heated to 75°C with stirring in 1 l of water, the pH is adjusted to 2.0 using hydrochloric acid, and 9.5 g of  $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$  are dissolved in the suspension. 7 g of TEOS (tetraethoxysilane) is added over the course of 10 minutes, the mixture is stirred for a further 30 minutes, and the pH is then adjusted to 6.5 over the course of 60 minutes.

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After a post-stirring time of 30 minutes, the post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 100 to 150°C, the pigment is calcined at 750°C for 45 minutes and sieved in accordance with the desired particle size.

15 The resultant pigment contains a coating of 2% of silicon dioxide and 2% of aluminium oxide.

### Organic post-treatment

20 100 g of the pretreated pigment are suspended in 1 l of water, the batch is heated to 75°C, and the pH is adjusted to 8.0 using hydrochloric acid or sodium hydroxide solution. 1.5 g of each of Dynasylan® AMMO, MEMO GLYMO are added over the course of 10 to 20 minutes. After a first post-stirring time of 30 minutes, 0.5 g of n-octyltrimethoxysilane is added, and stirring is continued for a further 30 minutes. The post-coated pigment is  
25 separated off from the supernatant by filtration and washed. After drying at 120 to 160°C, the pigment is sieved to a particle size of smaller than 40 µm.

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### Example 6

100 g of freshly rutile-coated glass flakes having a substrate thickness of less than 1 µm and a rutile content of 20%, based on the pigment, are



heated to 75°C with stirring in about 1.5 l of water, and the pH is adjusted to 9.0 using sodium hydroxide solution. 100 ml of a sodium water-glass solution having a silicic acid content of 5% are added over the course of 2 hours, during which the pH is kept constant by means of 2.5% sulfuric acid. The mixture is subsequently stirred for a further 30 minutes, and the pH is then adjusted to 7.5 over the course of 30 minutes using sulfuric acid.

After a post-stirring time of 30 minutes, the post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 100 to 150°C, the pigment is calcined at 700°C for 45 minutes and sieved in accordance with the desired particle size.

The resultant pigment contains a coating of 5% of silicon dioxide.

Organic post-treatment:

100 g of the pretreated pigment are suspended in 1 l of water, the batch is heated to 75°C, and the pH is adjusted to 8.0 using hydrochloric acid or sodium hydroxide solution. 2 g of each of the silanes Dynasylan® AMMO and GLYMO are added over the course of 10 to 20 minutes, and stirring is continued for a further 30 minutes. 2 g of Manchem C (carboxyzirconium aluminate from Rhone-Poulenc Chemicals) is subsequently added, and stirring is continued for 30 minutes. The post-coated pigment is separated off from the supernatant by filtration and washed. After drying at 120 to 160°C, the pigment is sieved to a particle size of smaller than 40 µm.

#### Comparative Example 1

100 g of the uncalcined base pigment described in Example 1 without aluminium oxide coating are suspended in 1 l of water, the batch is heated to 75°C, and the pH is adjusted to 8.0 using hydrochloric acid or sodium hydroxide solution. 2 g of each of the silanes Dynasylan® AMMO, MEMO and GLYMO are added over the course of 10 to 20 minutes, and stirring is subsequently continued for 60 minutes. The post-coated pigment is sepa-

rated off from the supernatant by filtration and washed. After drying at 120 to 160°C, the pigment is sieved to a particle size of smaller than 40 µm.

Comparative Example 2: [Eckart WO 99/57204 Example 10]

5 100 g of Iriodin® 103 are stirred for 10 min in 500 ml of ethanol. The suspension is warmed to 80°C, and a solution of 26 ml of 1N potassium hydroxide solution is added. After a further 5 minutes, 1 g of 3-methacryloxypropyltrimethoxysilane (MEMO) is added to the mixture. 30 min later, 10 2 g of trimethylolpropane trimethacrylate are added to the mixture, immediately followed by 30 mg of α,α'-azoisobutyronitrile. The entire batch is then stirred at 80°C for a further 4 h. The mixture is then allowed to cool, and the ready-coated pigment is filtered off with suction. Finally, the filter cake is dried at 90°C under reduced pressure.

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The pigments according to the invention and the pigments from the comparative examples were investigated by the following test methods:

**Photoactivity:**

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The pigment samples are incorporated into a plastic matrix, and the extent of the reduction of  $Pb^{2+}$  to Pb is determined visually. The assessment of the grey coloration is carried out in accordance with ISO 105-Part A 02 (corresponds to DIN 54 001). The test scale extends from 5 (very good) to 25 1 (very poor).

**Condensation water testing:**

30

The pigment samples are incorporated into a water-based coating system, and the test samples are produced by spray application.

The testing was carried out in accordance with DIN 50 017 (condensation water climates) for 1 hour and 4 hours after the end of the exposure. The test parameters are the adhesion (crosshatch, test scale from 0 (very good) to 5 (very poor), and the imaging sharpness (DOI, test scale from 10 (very good) to 0 (very poor)).

#### Results of the photostability and condensation water test:

The results of the photostability and condensation water tests are shown in the following table:

Sample	Photo-activity	Adhesion		DOI	
		1 h	4 h	1 h	4 h
1	3	1	0	5	8
2	3-4	0	0	4	7
3	3-2	1	0	5	8
4	3-2	1	0	6	9
5	3-2	1	0	6	8
6	3-2	0	0	4	7
C1	1	1	0	3	6
C2	2-1	1	0	5	8

Examples 1, C1 and C2 are silver pigments having a relatively low titanium dioxide content. These pigments, even without special post-treatment, are less photoactive compared with interference pigments having a higher rutile content (samples 2, 3 and 5). It is clearly evident that the inorganic post-coating enables a reduction in the photoactivity to be achieved.